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(54) LUMINOUS GLASS FORMED ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a luminous glass formed article without need for another energy source when light is emitted in the dark and having a high luminance at night by incorporating an aluminate phosphor of specified composition into the glass.

SOLUTION: This luminous glass formed article is provided with an afterglow phosphor shown by; $(M1-p-q, EupOp)O.n(Al1-mBm)2O3.kP2O5.\alpha X$ (for which $0.0001 \leq p \leq 0.5$, $0.0001 < q \leq 0.5$, $0.5 \leq m \leq 3.0$, $0 < m \leq 0.5$, $0 \leq k \leq 0.2$, $0 \leq \alpha \leq 0.5$, $0 \leq \alpha/m \leq 0.4$, M is Mg, Ca, Sr, Ba or Zn, Q is Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Y or Lu, and X is F, Cl, Br or I). A structure formed by kneading a phosphor into molten glass, a structure obtained by coating the lump of a phosphor or the lump coated with a phosphor or its surface and covered with glass, a structure formed by inserting a phosphor in glass in layers, etc., are exemplified as the formed article.

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CLAIMS

[Claim(s)]

[Claim 1] The noctilucent glass cast characterized by the afterglow nature fluorescent substance expressed by the following general formula inside transparency or a translucent glass cast possessing.
(M_{1-p-q}, E_pQ_q) O_n(aluminum_{1-mBm})₂O₃, kP₂O₅, and alphaX (however) It is in the range of 0.0001
 $\leq p \leq 0.50.0001$ $\leq q \leq 0.50.5$ $\leq n \leq 3.00$ $\leq m \leq 0.50$ $\leq k \leq 0.20$ $\leq \alpha \leq 0.50$ $\leq \alpha/n \leq 0.4$. However, M in an empirical formula is at least one sort chosen from the group of the divalent metal which consists of Mg, calcium, Sr, Ba, and Zn. Q is co-activating agent, and is at least one sort chosen from the group which consists of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and X is at least one sort chosen from the first the halogen origin which consists of F, Cl, Br, and I.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the glass cast in which noctilucent nature is shown.

[0002]

[Description of the Prior Art] There was nothing with the noctilucent function which emits light itself in darkness in the conventional glass cast. Although there was a glass ingredient which carries out solid-state luminescence, there was no cheap glass cast which a certain operation from the outside, such as electric field or a field, is needed at the time of luminescence, and does not need other energy sources. If the glass cast which has such a property is realizable, it can be used also for the application which needs safety, the application which needs energy saving, or the decorative object, and the application to the direction of many is expected.

[0003] As the way of thinking for realizing this, the luminous energy of the natural light or artificial illumination was once conserved, and there was a method of using the so-called noctilucent ingredient which this is released [ingredient] gradually and makes it emit light. However, since the conventional noctilucent ingredient be use zinc sulfide (ZnS) as a crystal parent, even if it oxidized simply at the elevated temperature at the time of glass processing, host crystal be destroyed, and it lost noctilucent nature and be able to process it at low temperature comparatively, originally this kind of noctilucent ingredient have low brightness, be boil further, have a fault, like degradation by ultraviolet rays be very large, and be able to bear practical use at all.

[0004]

[Problem(s) to be Solved by the Invention] This invention aims at offering the glass cast which does not need other energy sources at the time of luminescence in darkness and which has noctilucent nature with high brightness.

[0005]

[The means for solving invention] In order to solve the problem mentioned above, as a result of inquiring wholeheartedly, by making the interior of glass contain the aluminate fluorescent substance of a specific presentation, this invention person etc. finds out that a technical problem is solvable, and came to complete this invention.

[0006] That is, the noctilucent glass cast of this invention is characterized by the afterglow nature fluorescent substance expressed by the following general formula inside transparency or a translucent glass cast possessing.

(M_{1-p-q}, E_pQ_q)O_n(aluminum_{1-mBm})₂O₃, kP₂O₅, and alphaX (however) It is in the range of 0.0001 <= p <= 0.50.0001 <= q <= 0.50.5 <= n <= 3.00 <= m <= 0.50 <= k <= 0.20 <= alpha <= 0.50 <= alpha/n <= 0.4. However, M in an empirical formula is at least one sort chosen from the group of the divalent metal which consists of Mg, calcium, Sr, Ba, and Zn. Q is co-activating agent, and is at least one sort chosen from the group which consists of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and X is at least one sort chosen from the first the halogen origin which consists of F, Cl, Br, and I.

[0007] With the glass cast as used in the field of this invention, it is not necessarily restricted to that by which glass molding was carried out using the mold, but the approach ordinarily performed by glass industry or glass technology can be applied. That is, the structure where the lump which covered the afterglow nature fluorescent substance on the lump or front face of the structure and the afterglow nature fluorescent substance which scoured the afterglow nature fluorescent substance on the glass of a melting condition, put into the glass mold in the state of lump distribution, and were cast was covered with glass, the sandwich structure whose afterglow nature fluorescent substance was pinched in the shape of a layer with glass are fundamentally possible.

[0008] Furthermore, such primary operation articles are reheated and things to do for secondary elaboration, such as a press, hauling, or bending, are also possible.

[0009] The melting point of an afterglow nature fluorescent substance is very high compared with the temperature (1700-1800 degrees C and about 1000 degrees C) of glass, and, for the reason, an afterglow nature fluorescent substance does not deteriorate in glass working temperature extent.

[0010] In this invention, especially an important thing is the structure which the afterglow nature fluorescent substance

in a glass cast can receive outdoor daylight, and can emit light in afterglow. Then, especially as for glass, transparency or a translucent thing is required from the field of luminous efficiency.

[0011] The afterglow nature fluorescent substance used for the afterglow nature lamp of this invention can change a luminescent color tone substantially with the chemical composition. Chemical composition is the fluorescent substance which made the subject the aluminate activated with divalent europium, especially, it is the range of $0.5 \leq n \leq 1.5$, and a fluorescence color and afterglow present an efficient blue system as the 70-100-mol range of divalent metal M is % about calcium. The crystal structure of this afterglow nature fluorescent substance makes monoclinic system a subject, and is excited by the ultraviolet rays and the visible ray 420nm or less of the wavelength range.

[0012] If the above-mentioned chemical composition occupies divalent metal M and Sr occupies the 70-100-mol range of % in $0.5 \leq n \leq 1.5$, a fluorescence color and an afterglow color will present an efficient green system. The crystal structure of this afterglow nature fluorescent substance makes monoclinic system a subject, and is excited by the ultraviolet rays and the visible ray of the wavelength range of 500nm or less of **.

[0013] The range of the above-mentioned chemical composition is $1.5 < n \leq 3.0$, and when Sr occupies the 80-100-mol range of % for divalent metal M, a fluorescence color and an afterglow color are bluish green color systems. The crystal structure of this afterglow nature fluorescent substance makes orthorhombic system a subject, and is excited by the ultraviolet rays and the visible ray 460nm or less of the wavelength range. The host crystal of this fluorescent substance has the features that it is strong to chemical stability, such as thermal resistance and a water resisting property, especially, compared with the aluminate fluorescent substance which makes monoclinic system a subject, and is the best for the noctilucent glass mold goods of this invention.

[0014] The activator and co-activating agent which are introduced into an afterglow nature fluorescent substance influence a fluorescence color and afterglow brightness greatly. Practically, it adjusts to the range as shown below, respectively.

[0015] About the concentration p of Eu of an activator, 0.0001 mols or more of Sr of a parent are adjusted to the range permuted 0.5 mols or less to one mol of fluorescent substances. It is because lifting afterglow brightness will fall concentration quenching if optical absorption will worsen if fewer than 0.0001 mols, afterglow brightness becomes low as a result and it increases more than 0.5 mols conversely. The still more desirable range of p is that of $0.001 \leq p \leq 0.06$, and afterglow brightness becomes still higher in this range.

[0016] Luminescence of Eu comes to show afterglow nature by introducing co-activating agent. it was chosen out of the group which consists of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu as co-activating agent -- a kind is effective at least.

[0017] Especially Dy is effective on an afterglow disposition, when divalent metal M of a fluorescent substance parent is Sr, and the optimum density range of the Dy concentration q is 0.0005 or more and 0.03 or less range.

[0018] Especially Nd has effectiveness especially in the improvement in afterglow brightness, when divalent metal M of a fluorescent substance parent is calcium, and the optimal range of the Nd concentration q is 0.0005 or more and 0.03 or less range.

[0019] The synergistic effect is demonstrated by 2nd activating other co-activating agent to these co-activating agent Dy and Nd.

[0020] When choosing Dy as the first co-activating agent, the range where the Mn concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0005 or more and 0.02 or less range is still more desirable.

[0021] When choosing Dy as the first co-activating agent, the range where the Tm concentration q of the 2nd co-activating agent is desirable is 0.0003 or more and 0.02 or less, and 0.0004 or more and 0.01 or less range is still more desirable.

[0022] When choosing Dy as the first co-activating agent, the range where the Lu concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0004 or more and 0.04 or less range is still more desirable.

[0023] When choosing Dy as the first co-activating agent, the range where the Nb concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.08 or less, and 0.0003 or more and 0.04 or less range is still more desirable.

[0024] When choosing Dy as the first co-activating agent, the range where the Yb concentration q of the 2nd co-activating agent is desirable is 0.0002 or more and 0.04 or less, and 0.0003 or more and 0.01 or less range is still more desirable.

[0025] When choosing Dy as the first co-activating agent, the range where the Zr concentration q of the 2nd co-activating agent is desirable is 0.002 or more and 0.70 or less.

[0026] When choosing Dy as the first co-activating agent, the range where the Er concentration q of the second co-activating agent is desirable is 0.0001 or more and 0.03 or less. Furthermore, 0.0005 or more and 0.02 or less range is desirable.

[0027] When choosing Dy as the first co-activating agent, the range where the Pr concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.04 or less. Furthermore, 0.0005 or more and 0.03 or less range is desirable.

[0028] When introducing Nd as the first co-activating agent, the range where the Tm concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0005 or more and 0.02 or less range is still more desirable.

[0029] When introducing Nd as the first co-activating agent, the range where the Pr concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0005 or more and 0.02 or less range is still more desirable.

[0030] When introducing Nd below as the first co-activating agent, the range where the Ho concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0005 or more and 0.02 or less range is still more desirable.

[0031] When introducing Nd below as the first co-activating agent, the range where the Dy concentration q of the 2nd co-activating agent is desirable is 0.0001 or more and 0.06 or less, and 0.0005 or more and 0.02 or less range is still more desirable.

[0032] By adding and calcinating a halogen as flux, this afterglow nature fluorescent substance controls the particle growth with an unusual afterglow nature fluorescent substance, and becomes controllable about crystal growth. This is because a fluorescent substance particle comes to be calcinated by homogeneity by a halogen reacting with the aluminum which is the configuration element of a fluorescent substance, alkaline earth metal, a rare earth metal, etc., existing, and being calcinated. [especially on a fluorescent substance particle front face] [many] Consequently, it is improved and dispersibility of particle shape improves. independent [in the ammonium salt of halogens, such as ammonium fluoride (NH₄F), an ammonium chloride (NH₄Cl), an ammonium bromide (NH₄Br), and ammonium iodide (NH₄I), the halogenide of an alkaline earth element, aluminum halide, etc.] as a halogenated compound added as flux at the time of baking of an afterglow nature fluorescent substance -- or it is mixed and used. Most added halogens are altogether contained in a fluorescent substance presentation. Therefore, a content is controllable by mixing and calcinating the amount it is wished wants a fluorescent substance to contain in a raw material.

[0033] Depending on a fluorescent substance presentation, especially, depending on a mol several n [of the ** ulmin acid in the empirical formula of the afterglow nature fluorescent substance of this invention] value, when the value of n is [alkaline earth metal] Sr in 0.5 or more and 1.5 or less range, in the case of green and calcium, the luminescent color shows blue, as for the range of alpha, 0.003 or more and 0.2 or less are desirable, and, as for the luminescent color, as for the halogen content alpha, 0.05 or less and 0.12 or more are more desirable. Moreover, the value of n shows a bluish green color in 1.5 or more and 3.0 or less range, as for the range of alpha, 0.004 or more and 0.25 or less are desirable, and 0.08 or less and 0.15 or more are more desirable [as for luminescence]. Especially the 0.07 neighborhoods have [0.001 or more / 0.4 or less] the value of alpha/n most desirable [furthermore,].

[0034] By making the presentation of this afterglow nature fluorescent substance contain boron, crystallinity can be improved as a ** ulmin acid and it works effective in a raise in ** of afterglow brightness by the ability of an emission center and a trapping center to be stabilized. In order to introduce boron into a presentation, the method of adding and calcinating the compound containing boron is effective, the borate of boric acid or an alkaline earth element can be used, and especially boric acid is desirable. Most added boron is altogether contained in a fluorescent substance presentation. 0.0001 or more and 0.5 or less range is [the amount m of boron by which addition of boron permutes aluminum] desirable, 0.005 or more and 0.25 or less range is more desirable, and the 0.05 neighborhoods are the most desirable.

[0035] By making the boric acid and the phosphoric acid of the amount of specification contain simultaneously, the great portion of added boric acid makes an alumina and mixed crystal, it is included in a fluorescent substance presentation, and, as a result, the thermal resistance of a fluorescent substance improves. Superfluous boric acid has the work which makes a phosphoric-acid compound, and divalent metal and mixed crystal, and prevents the melting reaction between fluorescent substance particles. This mixed crystal has a water resisting property, in order to cover the particle front face of an afterglow nature fluorescent substance with insolubility in water. In order to introduce a phosphoric acid into a fluorescent substance parent, the phosphate of a phosphoric acid, a phosphoric anhydride, ammonium phosphate, and an alkaline earth element etc. can use it preferably as a raw material. Most added phosphoric acids are altogether contained in a fluorescent substance presentation. The phosphoric-acid concentration k in a fluorescent substance empirical formula has 0.001 or more and 0.2 or less desirable range, its 0.01 or more and 0.1 or less range is still more desirable, and its 0.03 or more and 0.05 or less range is [addition of a phosphoric-acid compound] the most desirable.

[0036] After calcinating the primary raw material which mixed these constituents and flux in atmospheric air for several hours at 1200-degree-C or more temperature of 1600 degrees C or less, the second bake is carried out in weak reducing atmosphere at or more 1200 the temperature of 1600 degrees C or less, and the afterglow nature fluorescent

substance of this invention is obtained by grinding and carrying out a screen in the obtained burned product. The mixed ratio of the raw material for acquiring the target afterglow nature fluorescent substance presentation is mostly in agreement with a theoretical ratio.

[0037]

[Example] Green luminescence used for the nohilucence glass cast of this invention, blue luminescence, and a bluish green color luminescence afterglow nature fluorescent substance can be prepared, for example by the following approaches.

[0038] As a [preparation of green system afterglow nature fluorescent substance] fluorescent substance raw material, SrCO₃ 140.98g (0.955 mols), 88.14g (0.865 mols) and Eu₂O₃ for aluminum 2O₃ 5.28g (0.015 mols), 2.80g (0.0075 mols) and H₃BO₃ for Dy2O₃ 5.63g (0.091 mols), And (NH₄) it puts into the ceramic pot of entering [HPO /4 / 2/g / (0.060 mols) / 7.92] alumina balls as a mixed medium, and mixes with a roller for 2 hours, and the mixed raw material before fluorescent substance baking (henceforth raw material student powder) is obtained. Next, raw material student powder is put into an alumina crucible, it calcinates at 1400 degrees C under reducing atmosphere for 5 hours, and a fluorescent substance burned product is obtained. Next, a burned product is ground and through and 200-0.91 (Sr_{0.955}Eu_{0.03}Dy_{0.015}) (aluminum 0.95B0.05) 2O₃.0.03P5 fluorescent substance are obtained for the screen of 200 meshes. This fluorescent substance shows luminescence of a green system with the high visibility which has a luminescence peak in 515nm.

[0039] As a [preparation of blue system afterglow nature fluorescent substance] fluorescent substance raw material, CaCO₃ 95.59g (0.955 mols), 94.01g (0.922 mols) and Eu₂O₃ for aluminum 2O₃ 2.64g (0.0075 mols), 5.05g (0.015 mols) and H₃BO₃ for Nd2O₃ 6.00g (0.097 mols), And (NH₄) it puts into the ceramic pot of entering [HPO /4 / 2/g / (0.060 mols) / 7.92] alumina balls as a mixed medium, and mixes with a roller for 2 hours, and raw material student powder is obtained. Next, raw material student powder is put into an alumina crucible, it calcinates at 1400 degrees C under reducing atmosphere for 5 hours, and a fluorescent substance burned product is obtained. Next, a burned product is ground and through and 200-0.97(calcium0.955Eu0.015Nd0.03) (aluminum 0.95B0.05) 2O₃.0.03P5 fluorescent substance are obtained for the screen of 200 meshes. This fluorescent substance shows luminescence of the blue system which has a luminescence peak in 420nm.

[0040] As a [preparation of bluish green system afterglow nature fluorescent substance] fluorescent substance raw material, SrCO₃ 140.98g (0.955 mols), 169.40g (1.663 mols) and Eu₂O₃ for aluminum 2O₃ 5.28g (0.015 mols), 2.80g (0.0075 mols) and H₃BO₃ for Dy2O₃ 10.8g (0.175 mols), And (NH₄) it puts into the ceramic pot of entering [HPO /4 / 2/g / (0.060 mols) / 7.92] alumina balls as a mixed medium, and mixes with a roller for 2 hours, and raw material student powder is obtained. Next, raw material student powder is put into an alumina crucible, it calcinates at 1400 degrees C under reducing atmosphere for 5 hours, and a fluorescent substance burned product is obtained. Next, a burned product is ground and through and 200-1.75(Sr_{0.955}Eu_{0.03}Dy_{0.015}) (aluminum 0.95B0.05) 2O₃.0.03P5 fluorescent substance are obtained for the screen of 200 meshes. This fluorescent substance shows luminescence of the bluish green system which has a luminescence peak in 490nm.

[0041] [Example 1] The example in the case of blowing and making a nohilucence glass cast according to glass technique is shown. Make crystal glass (BX[by triple-purpose industrial incorporated company]- 25) into a melting condition in a 1280-degree C furnace 25%, the cylinder of suitable amount iron blows it, and it is made to adhere at the head of a rod, and takes. The above-mentioned afterglow nature fluorescent substance is rolled on a griddle, the 900-1000-degree C glass which is soft is rolled every suitable amount and on it, and an afterglow nature fluorescent substance is attached to glass. It puts in into the melting glass in a furnace in order to roll glass further besides and to make an afterglow nature fluorescent substance into sandwich structure, and glass is twisted further. Next, it is made to expand, playing the melting glass which has adhered at a head and blowing a breath from the opposite hand of a rod, a form is prepared using the usual technique, and it is processed into a cop, an ash pan, a flower vase, etc. The nohilucence glass tumbler obtained by this example has structure whose afterglow nature fluorescent substance layer the interior pinched as it shows the sectional view to drawing 1.

[0042] what mixed crystal glass powder with the afterglow nature fluorescent substance by the weight ratio 1:1 25% is placed on a griddle in order to strengthen adhesive strength of [example 2] glass and an afterglow nature fluorescent substance, and except it, the same approach as an example 1 is enforced and it is sandwich structure ***** about an afterglow nature fluorescent substance in glass -- the nohilucence glass cast was obtained.

[0043] The glass which blew and became soft at the elevated temperature at the head of a rod in order to scour an afterglow nature fluorescent substance is attached into [example 3] glass, and a fluorescent substance is attached to it, and with a reheating furnace, it is made soft and twists. It wound with melting glass new besides, the afterglow nature fluorescent substance was confined in glass, it was processed by the usual technique, and the nohilucence glass paperweight shown in drawing 2 was made.

[0044] [Example 4] To the glass tumbler obtained by the usual glass technique, it paints using what mixed with the organic binder the blue glazing color used for enamel muffle painting, and a blue afterglow nature fluorescent

substance. It heated after a pattern's drying for about 1 hour at the furnace which is 580 degrees C, and the cop which performed enamel processing of noctilucent nature to the cop front face was obtained.

[0045] [Example 5] crystal glass powder and the powder which mixed the afterglow nature fluorescent substance by the weight ratio 10:1 were put into the 1100-degree C furnace, and it considered as the melting condition, and it was slushed into the mold, and it cooled, and took out from the mold, and the noctilucent glass tumbler which the afterglow nature fluorescent substance as shown in drawing 3 is distributing uniformly on glass was obtained.

[0046] A nitrocellulose / butyl-acetate binder is made to suspend a [example 6] afterglow nature fluorescent substance, suspension is applied to sheet glass, desiccation baking is carried out, and a fluorescent substance layer is formed on sheet glass. Sheet glass was placed on the fluorescent substance layer, and the noctilucent sheet glass cast shown in drawing 4 which put into the 800-degree C furnace under the vacua, and made the afterglow nature fluorescent substance sandwich structure was obtained. If this thing is used for a windowpane, light energy will be stored in an afterglow nature fluorescent substance by day-ranges sunlight, and a windowpane will emit light over long duration night.

[0047] [Example 7] The afterglow nature fluorescent substance was mixed with the polyvinyl butyral by the usual approach, it considered as the high polymer film, it was put between sandwich structure between two sheet glass, it heated at 300 degrees C with the vacuum furnace, and the noctilucent sheet glass cast which dissolves a high polymer film and is shown in drawing 5 was obtained. Although this example can also be used for the same application as an example 6, the direction depended on this example can obtain a noctilucent sheet glass cast by low cost more.

[0048] In the [example 8] example 6, completely transparent noctilucent sheet glass was able to be obtained by using the sheet glass prepared so that a refractive index might become the same value as an afterglow nature fluorescent substance.

[0049] [Example 9] On the flat surface of 1200-degree C melting tin, glass powder and the powder of an afterglow nature fluorescent substance were mixed to 10:1, and the glass melt on the flat surface of a melting condition was produced thoroughly. The noctilucent sheet glass which the afterglow nature fluorescent substance shown in drawing 6 distributed to homogeneity by this was obtained.

The noctilucent sheet glass of transparency was thoroughly obtained like the example 9 except doubling with the powder of an afterglow nature fluorescent substance the refractive index of the glass powder which carries out a [example 10] activity.

[0050] The internal hollow part of a glass tube is filled up with an afterglow nature fluorescent substance for soda glass with a [example 11] outer diameter [of 5mm], and a bore of 3mm, the end side of a glass tube is inserted into an electric furnace, and it heats at 650 degrees C. The pincette drew out the head, the place which the edge has softened with heating was connected with drawing equipment, and the noctilucent glass fiber with a diameter of about 0.2mm shown in drawing 7 was made to form continuously.

[0051] The noctilucent glass fiber obtained in the [example 12] example 11 was cut in die length of about 5mm, and it calcinated, supplying an air current from the lower part, as it has been residence-time 2 - 3 seconds in the 1200-degree C tube furnace which is carrying out opening of the fragment in the vertical direction, and the noctilucent glass bead shown in drawing 8 which became a globular form by baking was taken out from the tube furnace lower part.

[0052] The noctilucent sheet glass produced in examples 6-11 gives secondary molding of bending by the next reheating process, hauling, press molding, etc., and processing of a still freer configuration is possible for it.

[0053] About each product of these examples, the in the dark one after the bottom 5-minute exposure of sunlight showed luminescence which can be checked by looking for 6 hours. Compared with other green and a blue afterglow nature fluorescent substance, the afterglow of the noctilucent glass cast which used the bluish green color system afterglow nature fluorescent substance about what is processed especially at an elevated temperature 1000 degrees C or more was high brightness.

[0054] Although the conventional ZnS:Cu fluorescent substance was chosen as a [example of comparison] afterglow nature fluorescent substance and the noctilucent glass cast was produced by the same approach as examples 1-11, all the fluorescent substances denaturalized at the time of heating, and luminescence was thoroughly lost about what is processed especially at an elevated temperature 800 degrees C or more.

[Effect of the Invention] As explained above, the noctilucent glass cast of this invention name can show the noctilucent nature of high brightness which is not looked at by the conventional glass cast, and can give noctilucent nature to many kinds, such as lighting fitting, accessories, a handicraft, a structural windowpane, and a windowpane for cars, of glass casts by the application.

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(54)【発明の名称】夜光ガラス成型品

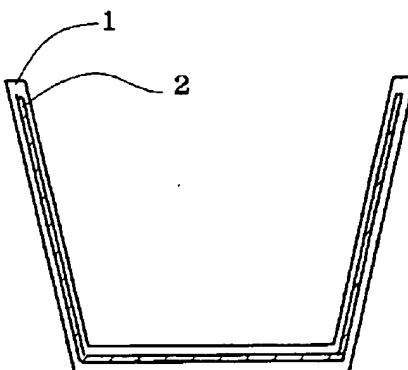
(57)【要約】

【目的】暗闇での発光時に他のエネルギーを源を必要としない、輝度の高い夜光性を有するガラス成型品を得る。

【構成】透明或いは半透明ガラス成型品の内部に次の二般式で表現される残光性蛍光体が具備されていることを特徴とする夜光ガラス成型品。

(M_{1-p-q}, E_{upQq}) O_n (A_{11-mBm}) 2O₃ · k P₂O₅ · α X

(ただし、0.0001 ≤ p ≤ 0.5 0.0001 ≤ q ≤ 0.5 0.5 ≤ n ≤ 3.0 0 < m ≤ 0.5 0 ≤ k ≤ 0.2 0 ≤ α ≤ 0.5 0 ≤ α / n ≤ 0.4 の範囲にあり、ただし、組成式中のMはMg、Ca、Sr、Ba、及びZnからなる2価金属の群より選ばれた少なくとも1種であり、Qは共付活剤でありMn、Zr、Nb、Pr、Nd、Gd、Tb、Dy、Ho、Er、Tm、Yb、及びLuからなる群より選ばれた少なくとも1種であり、XはF、Cl、Br、Iからなるハロゲン元素より選ばれた少なくとも1種である。)



【特許請求の範囲】

【請求項1】 透明或いは半透明ガラス成型品の内部に次の一般式で表現される残光性蛍光体が具備されていることを特徴とする夜光ガラス成型品。

(M_{1-p-q}, E_{upQq}) O · n (A_{11-mBm}) 2O₃ · k
P₂O₅ · α X

(ただし、 0.0001 ≤ p ≤ 0.5

0.0001 ≤ q ≤ 0.5

0.5 ≤ n ≤ 3.0

0 < m ≤ 0.5

0 ≤ k ≤ 0.2

0 ≤ α ≤ 0.5

0 ≤ α/n ≤ 0.4 の範囲にあり、

ただし、組成式中のMはMg、Ca、Sr、Ba、及びZnからなる2価金属の群より選ばれた少なくとも1種であり、Qは共付活剤でありMn、Zr、Nb、Pr、Nd、Gd、Tb、Dy、Ho、Er、Tm、Yb、及びLuからなる群より選ばれた少なくとも1種であり、XはF、Cl、Br、Iからなるハロゲン元素より選ばれた少なくとも1種である。)

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は夜光性を示すガラス成型品に関する。

【0002】

【従来の技術】従来のガラス成型品には、暗闇で自ら発光する夜光機能を持ったものはなかった。固体発光するガラス材料はあるが、発光時には電界或いは磁界等の外部からの何らかの作用が必要とされ、他のエネルギー源を必要としない安価なガラス成型品はなかった。このような特性を有するガラス成型品を実現することができれば、安全性を必要とする用途、省エネルギーを必要とする用途、或いは装飾的な目的にも使用でき、多方面への応用が期待される。

【0003】これを実現するための発想として、自然光或いは人工照明の光のエネルギーを一旦蓄え、これを徐々に解放し発光させるいわゆる夜光材料を利用する方法があった。しかし、従来の夜光材料は結晶母体として硫化亜鉛(ZnS)を使用しているため、ガラス加工時の高温で簡単に酸化され母体結晶が破壊され、夜光性を失い、また、比較的低温で加工できたとしても、この種の夜光材料は本来輝度が低く、さらにに紫外線による劣化が極めて大きいなどの欠点を有し、全く実用に耐えられなかつた。

【0004】

【発明が解決しようとする課題】本発明は暗闇での発光時に他のエネルギー源を必要としない、輝度の高い夜光性を有するガラス成型品を提供することを目的とする。

【0005】

【発明を解決するための手段】本発明者等は上述した問

題を解決するために鋭意検討した結果、ガラスの内部に特定組成のアルミニン酸塩蛍光体を含有させることにより、課題を解決できることを見いだし、本発明を完成させるに至った。

【0006】すなわち、本発明の夜光ガラス成型品は、透明或いは半透明ガラス成型品の内部に次の一般式で表現される残光性蛍光体が具備されていることを特徴とする。

(M_{1-p-q}, E_{upQq}) O · n (A_{11-mBm}) 2O₃ · k
P₂O₅ · α X

(ただし、 0.0001 ≤ p ≤ 0.5

0.0001 ≤ q ≤ 0.5

0.5 ≤ n ≤ 3.0

0 < m ≤ 0.5

0 ≤ k ≤ 0.2

0 ≤ α ≤ 0.5

0 ≤ α/n ≤ 0.4 の範囲にあり、ただし、組成式中のMはMg、Ca、Sr、Ba、及びZnからなる2価金属の群より選ばれた少なくとも1種であり、Qは共付活剤でありMn、Zr、Nb、Pr、Nd、Gd、Tb、Dy、Ho、Er、Tm、Yb、及びLuからなる群より選ばれた少なくとも1種であり、XはF、Cl、Br、Iからなるハロゲン元素より選ばれた少なくとも1種である。)

【0007】本発明でいうガラス成型品とは、型を用いてガラス成型されたものに必ずしも限られず、ガラス工業、或いはガラス工芸で普通に行われる方法が適用可能である。すなわち、溶融状態のガラスに残光性蛍光体を練り込み分散状態でガラス型に入れて成型された構造、

【0008】さらに、これらの一次加工品を再加熱しプレス、引っ張り、或いは曲げなどの2次加工することも可能である。

【0009】残光性蛍光体の融点は1700～1800°Cと、ガラスの1000°C程度の温度に比べて極めて高く、その為、ガラス加工温度程度では残光性蛍光体が変質することはない。

【0010】本発明において特に重要なのは、ガラス成型品の中の残光性蛍光体が外光を受光でき、残光を発光できる構造であることである。それで、発光効率の面から特にガラスは透明或いは半透明であることが要求される。

【0011】本発明の残光性ランプに用いる残光性蛍光体は、その化学組成により、発光色調を大幅に変えることができる。化学組成は2価のユーロピウムで付活されたアルミニン酸塩を主体とした蛍光体であり、特に、0.5 ≤ n ≤ 1.5 の範囲で、2価金属MがCaを70～1

0.0モル%の範囲であると蛍光色、及び残光は高効率の青色系を呈する。この残光性蛍光体の結晶構造は単斜晶系を主体とし、420nm以下の波長範囲の紫外線及び可視光線により励起される。

【0012】上記化学組成が $0.5 \leq n \leq 1.5$ の範囲で、2価金属MをSrが70~100モル%の範囲を占めると蛍光色、及び残光色は高効率の緑色系を呈する。この残光性蛍光体の結晶構造は単斜晶系を主体とし、は500nm以下の波長範囲の紫外線及び可視光線により励起される。

【0013】上記化学組成が $1.5 < n \leq 3.0$ の範囲で、2価金属MをSrが80~100モル%の範囲を占めると蛍光色、及び残光色は青緑色系である。この残光性蛍光体の結晶構造は斜方晶系を主体とし、460nm以下の波長範囲の紫外線及び可視光線により励起される。この蛍光体の母体結晶は、単斜晶系を主体とするアルミニ酸塩蛍光体に比べると、特に、耐熱性、耐水性等の化学安定性に強いという特長を持ち、本発明の夜光ガラス成形品には最適である。

【0014】残光性蛍光体に導入する付活剤および共付活剤は、蛍光色および残光輝度に大きく影響する。実用上、それぞれ次に示すような範囲に調整する。

【0015】付活剤のEuの濃度pについては、蛍光体1モルに対し、母体のSrを0.0001モル以上、0.5モル以下置換する範囲に調整する。なぜなら0.0001モルより少ないと光吸収が悪くなり、その結果残光輝度が低くなり、逆に、0.5モルよりも多くなると、濃度消光を起こし残光輝度が低下するからだ。pのさらに好ましい範囲は $0.001 \leq p \leq 0.06$ のであり、この範囲で残光輝度がさらに高くなる。

【0016】共付活剤を導入することによりEuの発光は残光性を示すようになる。共付活剤としてMn、Zr、Nb、Pr、Nd、Gd、Tb、Dy、Ho、Er、Tm、Yb、及びLuからなる群より選ばれた少くとも一種が有効である。

【0017】Dyは蛍光体母体の2価金属Mが特にSrの場合に残光性向上に効果的であり、Dy濃度qの最適濃度範囲は0.0005以上、0.03以下の範囲である。

【0018】Ndは蛍光体母体の2価金属Mが特にCaの場合に残光輝度向上に特に効果があり、Nd濃度qの最適範囲は0.0005以上、0.03以下の範囲である。

【0019】これら共付活剤Dy、Ndに、他の第2に共付活剤を付活することにより相乗効果を發揮する。

【0020】第一の共付活剤としてDyを選択する場合、第2の共付活剤のMn濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.0005以上、0.02以下の範囲である。

【0021】第一の共付活剤としてDyを選択する場

合、第2の共付活剤のTm濃度qの好ましい範囲は0.0003以上、0.02以下で、更に好ましいのは0.0004以上、0.01以下の範囲である。

【0022】第一の共付活剤としてDyを選択する場合、第2の共付活剤のLu濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.0004以上、0.04以下の範囲である。

【0023】第一の共付活剤としてDyを選択する場合、第2の共付活剤のNb濃度qの好ましい範囲は0.

10 0001以上、0.08以下で、更に好ましいのは0.0003以上、0.04以下の範囲である。

【0024】第一の共付活剤としてDyを選択する場合、第2の共付活剤のYb濃度qの好ましい範囲は0.0002以上、0.04以下で、更に好ましいのは0.0003以上、0.01以下の範囲である。

【0025】第一の共付活剤としてDyを選択する場合、第2の共付活剤のZr濃度qの好ましい範囲は0.002以上、0.70以下である。

20 【0026】第一の共付活剤としてDyを選択する場合、第二の共付活剤のEr濃度qの好ましい範囲は0.0001以上、0.03以下である。更に好ましいのは0.0005以上、0.02以下の範囲である。

【0027】第一の共付活剤としてDyを選択する場合、第2の共付活剤のPr濃度qの好ましい範囲は0.0001以上、0.04以下である。更に好ましいのは0.0005以上、0.03以下の範囲である。

【0028】第一の共付活剤としてNdを導入する場合、第2の共付活剤のTm濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.

30 0005以上、0.02以下の範囲である。

【0029】第一の共付活剤としてNdを導入する場合、第2の共付活剤のPr濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.0005以上、0.02以下の範囲である。

【0030】第一の共付活剤としてNdを以下導入する場合、第2の共付活剤のHo濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.0005以上、0.02以下の範囲である。

40 【0031】第一の共付活剤としてNdを以下導入する場合、第2の共付活剤のDy濃度qの好ましい範囲は0.0001以上、0.06以下で、更に好ましいのは0.0005以上、0.02以下の範囲である。

【0032】本残光性蛍光体は、フラックスとしてハロゲン元素を添加して焼成することにより、残光性蛍光体の異常な粒子成長を抑制し、結晶成長をコントロール可能となる。これは、ハロゲン元素が蛍光体の構成元素であるアルミニウム、アルカリ土類金属、希土類金属等と反応し、特に蛍光体粒子表面に多く存在して焼成されることで、蛍光体粒子が均一に焼成されるようになるからだ。その結果、粒子形状は改善され、分散性が向上す

る。残光性蛍光体の焼成時のフランクスとして添加するハロゲン化合物としては、フッ化アンモニウム (NH_4F)、塩化アンモニウム (NH_4Cl)、臭化アンモニウム (NH_4Br)、沃化アンモニウム (NH_4I) 等のハロゲン元素のアンモニウム塩、アルカリ土類元素のハロゲン化物、及びハロゲン化アルミニウム等を単独あるいは混合して使用する。添加したハロゲン元素は殆ど全て蛍光体組成に含有される。従って、蛍光体に含有させたいと願う量を原料に混合し焼成することで含有量をコントロールすることができる。

【0033】ハロゲン含有量 α は蛍光体組成に依存し、特に、本発明の残光性蛍光体の組成式中の硼アルミン酸のモル数 n の値に依存し、 n の値が 0.5 以上、1.5 以下の範囲において、アルカリ土類金属が Sr の場合発光色は緑色、Ca の場合発光色は青色を示し、 α の範囲は 0.003 以上、0.2 以下が好ましく、0.05 以下、0.12 以上がより好ましい。また、 n の値が 1.5 以上、3.0 以下の範囲において発光は青緑色を示し、 α の範囲は 0.004 以上、0.25 以下が好ましく、0.08 以下、0.15 以上がより好ましい。さらに、 α/n の値が 0.001 以上、0.4 以下、特に 0.07 付近が最も好ましい。

【0034】本残光性蛍光体の組成に硼素を含有させることにより、硼アルミン酸として結晶性を改善でき、発光中心と捕獲中心を安定化できることで残光輝度の高輝化に有効に働く。硼素を組成に導入する為には、硼素を含んだ化合物を加えて焼成する方法が有効で、硼酸あるいはアルカリ土類元素の硼酸塩が使用でき、特に硼酸が好ましい。添加した硼素は殆ど全て蛍光体組成に含有される。硼素の添加は、アルミニウムを置換する硼素量 m が 0.0001 以上、0.5 以下の範囲が好ましく、より好ましいのは 0.005 以上、0.25 以下の範囲で、最も好ましいのは 0.05 付近である。

【0035】特定量の硼酸とリン酸を同時に含有させることで、加えた硼酸の大半がアルミナと混晶を作り蛍光体組成に組み込まれ、その結果蛍光体の耐熱性が向上する。過剰の硼酸はリン酸化合物及び 2 値金属と混晶を作り蛍光体粒子間の溶融反応を防ぐ働きがある。この混晶は水に不溶性で残光性蛍光体の粒子表面を被覆するために耐水性を持つ。リン酸を蛍光体母体に導入するためには、原料としてリン酸、無水リン酸、リン酸アンモニウム、アルカリ土類元素のリン酸塩等が好ましく使用できる。添加したリン酸は殆ど全て蛍光体組成に含有される。リン酸化合物の添加は、蛍光体組成式中リン酸濃度 k は 0.001 以上、0.2 以下の範囲が好ましく、0.01 以上、0.1 以下の範囲がさらに好ましく、0.03 以上、0.05 以下の範囲が最も好ましい。

【0036】これら構成成分及びフランクスを混合した原料を、大気中で 1200°C 以上 1600°C 以下の温度で数時間 1 次焼成した後、弱還元雰囲気中で 1200 以

上 1600°C 以下の温度で 2 次焼成し、得られた焼成品を粉碎、篩することで本発明の残光性蛍光体が得られる。目的の残光性蛍光体組成を得る為の原料の混合比率は、理論比率とほぼ一致する。

【0037】

【実施例】本発明の夜光ガラス成型品に使用する緑色発光、青色発光、及び青緑色発光残光性蛍光体は、例えば次のような方法で調製することができる。

【0038】【緑色系残光性蛍光体の調製】

蛍光体原料として、SrCO₃を 140.98 g (0.955 mol)、Al₂O₃を 88.14 g (0.865 mol)、Eu₂O₃を 5.28 g (0.015 mol)、Dy₂O₃を 2.80 g (0.0075 mol)、H₃BO₃を 5.63 g (0.091 mol)、及び (NH₄)₂HPO₄を 7.92 g (0.060 mol) を、混合媒体としてアルミナボール入りのセラミックポットに入れ、ローラーで 2 時間混合し蛍光体焼成前混合原料（以下原料生粉という）を得る。次に、原料生粉をアルミナルツボに入れ、還元雰囲気下 1400°C で 5 時間焼成し蛍光体焼成品を得る。次に焼成品を粉碎し、200 メッシュの篩を通して、(Sr_{0.955}Eu_{0.03}Dy_{0.015})_{0.91}(Al_{0.95}Bo_{0.05})₂₀₃・0.03P₂O₅ 蛍光体を得る。この蛍光体は発光ピークが 515 nm にある視感度の高い緑色系の発光を示す。

【0039】【青色系残光性蛍光体の調製】

蛍光体原料として、CaCO₃を 95.59 g (0.955 mol)、Al₂O₃を 94.01 g (0.922 mol)、Eu₂O₃を 2.64 g (0.0075 mol)、Nd₂O₃を 5.05 g (0.015 mol)、H₃BO₃を 6.00 g (0.097 mol)、及び (NH₄)₂HPO₄を 7.92 g (0.060 mol) を、混合媒体としてアルミナボール入りのセラミックポットに入れ、ローラーで 2 時間混合し原料生粉を得る。次に、原料生粉をアルミナルツボに入れ、還元雰囲気下 1400°C で 5 時間焼成し蛍光体焼成品を得る。次に焼成品を粉碎し、200 メッシュの篩を通して、(Ca_{0.955}Eu_{0.015}Nd_{0.03})_{0.97}(Al_{0.95}Bo_{0.05})₂₀₃・0.03P₂O₅ 蛍光体を得る。この蛍光体は発光ピークが 420 nm にある青色系の発光を示す。

【0040】【青緑色系残光性蛍光体の調製】

蛍光体原料として、SrCO₃を 140.98 g (0.955 mol)、Al₂O₃を 169.40 g (1.663 mol)、Eu₂O₃を 5.28 g (0.015 mol)、Dy₂O₃を 2.80 g (0.0075 mol)、H₃BO₃を 10.8 g (0.175 mol)、及び (NH₄)₂HPO₄を 7.92 g (0.060 mol) を、混合媒体としてアルミナボール入りのセラミックポットに入れ、ローラーで 2 時間混合し原料生粉を得る。次に、原料生粉をアルミナルツボに入れ、還元雰囲気下 1400°C で 5 時間焼成し蛍光体焼成品を得る。次に焼成品を粉碎し、200 メッシュの篩を通して、(Sr_{0.955}Eu_{0.03}Dy_{0.01})_{0.91}(Al_{0.95}Bo_{0.05})₂₀₃・0.03P₂O₅ 蛍光体を得る。この蛍光体は発光ピークが 515 nm にある青緑色系の発光を示す。

5) 0.1.75(A10.95B0.05)203·0.03P205蛍光体を得る。この蛍光体は発光ピークが490 nmにある青緑系の発光を示す。

【0041】[実施例1] 吹きガラス技法に従い夜光ガラス成型品を作る場合の例を示す。25%クリスタルガラス(三徳工業株式会社製BX-25)を1280°Cの炉内で溶融状態とし、それを適量鉄製の筒の吹き棒の先端に付着させて取る。鉄板の上に上記残光性蛍光体を適量置き、その上に900~1000°Cの柔らかくなっているガラスを転がし、残光性蛍光体をガラスに付ける。この上にさらにガラスを巻いて残光性蛍光体をサンドイッチ構造とする目的で炉内の溶融ガラスの中に入れ、ガラスをさらに巻き付ける。次に先端に付着している溶融ガラスを吹き棒の反対側から息を吹き込みながら膨張させ、通常の技法を用いて形を整え、コップ、灰皿、花瓶等に加工する。本実施例で得られる夜光ガラスコップはその断面図を図1に示す通り、内部に残光性蛍光体層を挟んだ構造となっている。

【0042】[実施例2] ガラスと残光性蛍光体の接着力を強くする目的で、残光性蛍光体と25%クリスタルガラス粉を重量比1:1で混合したものを鉄板の上に置き、それ以外は実施例1と同じ方法を実施し、ガラス中に残光性蛍光体をサンドイッチ構造封じ込んだ夜光ガラス成型品を得た。

【0043】[実施例3] ガラスの中に残光性蛍光体を練り込む目的で、吹き棒の先端に高温で柔らかくなったガラスを付け、それに蛍光体を付け、再加熱炉で柔らかくしてねじる。この上に新たな溶融ガラスで巻いて残光性蛍光体をガラスに封じ込み、通常の技法により加工し、図2に示す夜光ガラス製文鎮に仕上げた。

【0044】[実施例4] 通常のガラス技法により得られたガラスコップに、エナメル絵付けに用いられる青色透明顔料と青色残光性蛍光体を有機バインダーに混ぜたものを用いて絵付けを行う。絵柄が乾燥後、580°Cの炉にて約一時間加熱し、コップ表面に夜光性のエナメル加工を施したコップを得た。

【0045】[実施例5] クリスタルガラス粉と残光性蛍光体を重量比で10:1で混合した粉を、1100°Cの炉に入れ溶融状態とし、それを型に流し込み、冷却して型から取りだし、図3に示すような残光性蛍光体がガラスに一様に分散している夜光ガラスコップを得た。

【0046】[実施例6] 残光性蛍光体をニトロセルロース/酢酸ブチルバインダーに懸濁させ、懸濁液を板ガラスに塗布し、乾燥焼成し蛍光体層を板ガラス上に形成する。蛍光体層の上に板ガラスを置き、真空状態下800°Cの炉に入れ残光性蛍光体をサンドイッチ構造とした図4に示す夜光板ガラス成型品を得た。このものを窓ガラスに使用すると、昼間太陽光により残光性蛍光体に光エネルギーを蓄え、夜は窓ガラスが長時間に渡り発光する。

【0047】[実施例7] 通常の方法により残光性蛍光体をポリビニルブチラールと混合し高分子フィルムとし、それを板ガラス2枚の間にサンドイッチ構造に挟み込み、真空炉で300°Cに加熱し、高分子フィルムを融解し図5に示す夜光板ガラス成型品を得た。本実施例も実施例6と同じ用途に使用することができるが、本実施例による方がより低コストで夜光板ガラス成型品を得ることができる。

【0048】[実施例8] 実施例6において、屈折率が残光性蛍光体と同じ値になるように調製された板ガラスを使用することにより、完全に透明な夜光板ガラスを得ることができた。

【0049】[実施例9] 1200°Cの溶融錫の平面の上に、ガラス粉と残光性蛍光体の粉を10:1に混合し、完全に溶融状態の平面上のガラス溶融物を作製した。これにより、図6に示す残光性蛍光体が均一に分散した夜光板ガラスを得た。

【0050】[実施例10] 使用するガラス粉の屈折率を残光性蛍光体の粉に合わせること以外実施例9と同様にして完全に透明の夜光板ガラスを得た。

【0051】[実施例11] 外径5mm、内径3mmのソーダガラスをガラス管の内空部に残光性蛍光体を充填し、ガラス管の一端側を電気炉内に挿入して650°Cに加熱する。端部が加熱により軟化してきたところをピンセットで先端を引き出し、延伸装置に連結し、図7に示す直径約0.2mmの夜光ガラス繊維を連続的に形成させた。

【0052】[実施例12] 実施例11で得られた夜光ガラス繊維を5mm程度の長さに切断し、その断片を上30下方向に開口している1200°Cの環状炉に滞留時間2~3秒となるように気流を下部から供給しながら焼成し、焼成により球形となった図8に示す夜光ガラスピーズを環状炉下部から取り出した。

【0053】これら実施例の各製品については、太陽光下5分照射後暗中で6時間視認可能な発光を示した。特に1000°C以上の高温で加工するものについては、青緑色系残光性蛍光体を使用した夜光ガラス成型品は、他の緑色、青色残光性蛍光体に比べ残光が高輝度であった。

【0054】[比較例] 残光性蛍光体として従来のZnS:Cu蛍光体を選択し、実施例1~11と同様の方法で夜光ガラス成型品を作製したが、加熱時に全ての蛍光体が変性し、特に800°C以上の高温で加工するものに関しては発光が完全に失われた。

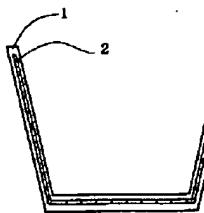
【発明の効果】以上説明したように、本発明名の夜光ガラス成型品は従来のガラス成型品に見られないような高

輝度の夜光性を示し、その応用により、照明器具、装飾品、工芸品、建築用窓ガラス、車両用窓ガラス等多くの種類のガラス成型品に夜光性を付与することができる。

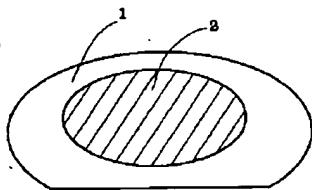
【図面の簡単な説明】

- 【図1】本発明に係る夜光ガラスコップの断面図。
- 【図2】本発明に係る夜光文鎮の断面図。
- 【図3】本発明に係る夜光ガラスコップの断面図。
- 【図4】本発明に係る夜光板ガラスの斜視図。

【図1】



【図2】



【図5】本発明に係る夜光板ガラスの斜視図。

【図6】本発明に係る夜光板ガラスの斜視図。

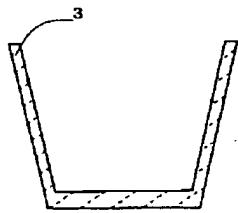
【図7】本発明に係る夜光板ガラス繊維の斜視図。

【図8】本発明に係る夜光ガラスピース断面図。

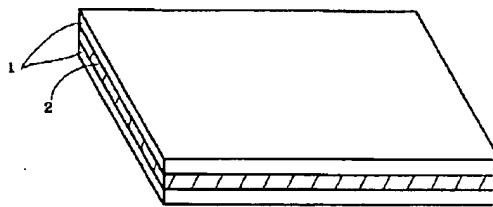
【符号の説明】

- 1 ····· ガラス
- 2 ····· 残光性蛍光体
- 3 ····· 残光性蛍光体を分散しているガラス

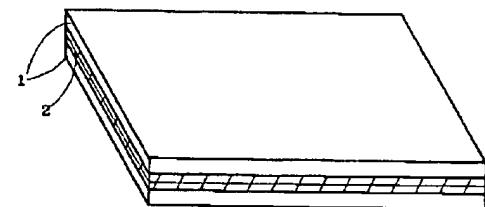
【図3】



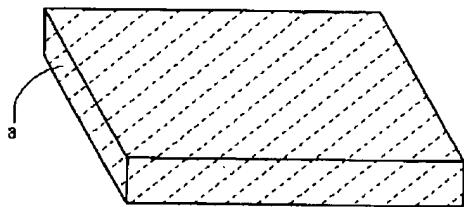
【図4】



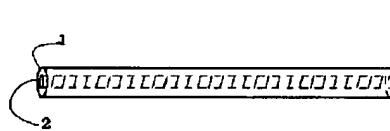
【図5】



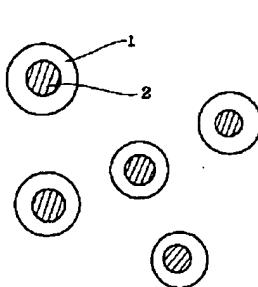
【図6】



【図7】



【図8】



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